

Pentafluorophenyl Alkyl and Vinyl Ethers¹

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The synthesis of various derivatives of pentafluorophenetole of the type $C_6F_5OCH_2CH_2R$ is described. The R group was chlorine, bromine, hydroxyl, pentafluorophenoxy, acetoxy, and trifluoroacetoxy. 2-Pentafluorophenoxy-1,1,1-trifluoroethane and 1,1-bis(pentafluorophenoxy)ethane were similarly synthesized. A study was made of the behavior of these ethers toward pyrolysis, acids, and bases. In general, those ethers containing β -hydrogen atoms give pentafluorophenol on pyrolysis. Some compounds, such as 2-pentafluorophenoxyethyl bromide, give rearranged products as well. Under basic conditions, cleavage to pentafluorophenol was observed with aqueous potassium hydroxide, whereas the use of solid potassium hydroxide pellets gives dehydrohalogenated products. Concentrated sulfuric acid causes cleavage of most of the ethers employed. 2-Pentafluorophenoxy-1,1,1-trifluoroethane resists attack both by acids and bases.

The synthesis and polymerization of two new vinyl monomers, pentafluorophenyl vinyl ether and 1,2-difluorovinyl pentafluorophenyl ether, are also presented.

Key Words: Ethers, pentafluorophenyl, pentafluorophenoxy, alkyl, vinyl, difluorovinyl, polymerization, and pyrolysis.

1. Introduction

In a previous report [1],² we have described the synthesis and polymerization of phenyl trifluorovinyl ether and pentafluorophenyl trifluorovinyl ether. Although these low molecular weight polymers were not exceptionally stable thermally, the complex mechanism by which these polymers decompose was of interest. To aid in the elucidation of this decomposition, two new monomers were synthesized—(1) pentafluorophenyl vinyl ether and (2) 1,2-difluorovinyl pentafluorophenyl ether. The pyrolysis of these polymers, along with that of model compounds, would yield information regarding the relative ease with which hydrogen fluoride or pentafluorophenol (probable breakdown products) are removed from various positions in the polymer chain as the possible first step leading to degradation.

2. Pentafluorophenyl Alkyl Ethers

The pentafluorophenyl alkyl ethers were synthesized as precursors to pentafluorophenyl vinyl ether. In the past, various derivatives of fluorinated anisoles [2-4] and phenetoles [3, 5] have been prepared by the nucleophilic alkoxide attack on hexafluorobenzene. Similarly, we have synthesized 2-pentafluorophenoxy-1,1,1-trifluoroethane from hexafluorobenzene and sodium trifluoroethoxide using tetrahydrofuran as the solvent. In an attempt to prepare 2-pentafluorophenoxyethyl bromide by this procedure, difficulties were encountered

in making the salt of 2-bromoethanol. Apparently, the salt readily decomposes to sodium bromide and ethylene oxide. However, 2-pentafluorophenoxyethyl bromide was conveniently synthesized by the reverse reaction, i.e., from potassium pentafluorophenoxide and 1,2-dibromoethane. This reaction was found to proceed more rapidly in *N,N*-dimethylformamide than in tetrahydrofuran. In this reaction, even though a large excess of dibromoethane was employed, a fair amount of 1,2-bis(pentafluorophenoxy)ethane was always isolated. By a similar reaction, attempts to prepare the isomeric 1-bromo-1-pentafluorophenoxyethane failed to yield any of this compound, only the 1,1-bis(pentafluorophenoxy)ethane being isolated. Apparently, when one pentafluorophenoxy group is attached to the carbon atom bearing the bromine atom, the remaining bromine atom is easily displaced by pentafluorophenoxide ion under the basic reaction-conditions. The fact that some free pentafluorophenol was obtained would seem to indicate that some of the pentafluorophenoxide was depleted, due to some dehydrohalogenation reaction.

In a like manner, 2-pentafluorophenoxyethyl chloride was prepared from 1,2-dichloroethane and potassium pentafluorophenoxide. Only the monochloro derivative was obtained in this reaction.

2-Pentafluorophenoxyethanol was also synthesized by this method from 2-bromoethanol and potassium pentafluorophenoxide, except that, in this case, tetrahydrofuran served satisfactorily as the reaction medium. This compound, 2-pentafluorophenoxyethanol, was recently [7] prepared from hexafluorobenzene and ethylene glycol in the presence of sodium hydroxide.

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² Figures in brackets indicate the literature references at the end of this paper.

Both the acetate and trifluoroacetate of 2-pentafluorophenoxyethanol were prepared in high yield by refluxing the alcohol and the appropriate anhydride for 1 hr.

Since pentafluorophenoxide is considered a weak nucleophile [4, 6], the choice of either tetrahydrofuran or *N,N*-dimethylformamide as the solvent for these reactions appears to depend on the relative activity of the halide to be replaced. For example, at 90 °C in *N,N*-dimethylformamide, the reaction between pentafluorophenoxide and 1,2-dibromoethane is essentially complete in a few hours, whereas the yield of product on refluxing in tetrahydrofuran for 18 hr was only 10 percent.

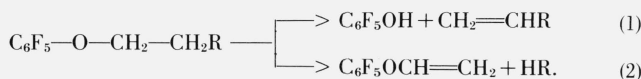
3. Pentafluorophenyl Vinyl Ether

Phenyl vinyl ether [8–10] and pentachlorophenyl vinyl ether [11–13] have been prepared previously, usually by the base-catalyzed addition of phenol or pentachlorophenol to acetylene. We have now extended this reaction to pentafluorophenol. Pentafluorophenyl vinyl ether can be prepared in 50 percent yield by this method. The reaction temperature was 200 °C, and a fair excess of acetylene was used to control the by-products, mainly 1,1-bis(pentafluorophenoxy)ethane. Previously, methanol [11] and water [12] were the preferred solvents. To prevent possible exchange reactions between potassium pentafluorophenoxide and protonic solvents at high temperature, we have used *N,N*-dimethylacetamide for this reaction with equal success.

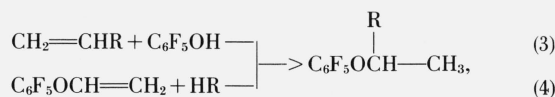
Although the above method for the synthesis of pentafluorophenyl vinyl ether was satisfactory, we have also investigated alternative methods of preparation. These methods included dehydrohalogenation or cleavage of various substituted alkyl ethers by pyrolytic means or basic reagents, or both. These reactions also gave valuable information regarding the relative stability of the fluoroaryl ethers under these conditions. Furthermore, these compounds may serve as model compounds in studying the decomposition products obtained from the pyrolysis of the polymeric fluoroaryl vinyl ethers.

4. Pyrolysis

The pyrolysis of a number of these fluoroaryl ethers having various substituents on the alkyl side-chain was performed in a flow system using glass helices, charcoal pellets, or 20 percent potassium hydroxide-charcoal pellets as the column packing. Temperatures ranged from 400 to 600 °C. Usually, atmospheric pressure was maintained, but in a few cases, the pyrolysis was done under reduced pressure. The conditions and the results of the pyrolyses of these pentafluorophenyl ethers are listed in table 1. For the most part, the pyrolyses appear to follow the paths as outlined in eqs 1 and 2.



In general, more pentafluorophenol than pentafluorophenyl vinyl ether was found in the pyrolyzates. The proportion of each compound appears to depend on the nature of the *R* group, as well as on the temperature employed in the pyrolysis. At no time have these pyrolyses shown any definite trend in any one direction, i.e., in preferred scission to pentafluorophenol (except where no β -hydrogen atoms are present) or pentafluorophenyl vinyl ether. The distribution of products seems to indicate that random scissions occur according to eqs 1 and 2. The pyrolysis products were further complicated by competing secondary reactions, which appeared to yield products which were simple addition products of the olefin formed from the initial pyrolysis, as shown in eqs 3 and 4 (or various combinations thereof),



This was especially evident in the case of the bromine derivative (table 1, *R*=Br). The large proportion of 1-bromo-1-pentafluorophenoxyethane formed in this pyrolysis would seem to indicate that both types of reaction (eqs 3 and 4) had occurred.

TABLE 1. Pyrolysis of $\text{C}_6\text{F}_5\text{OCH}_2\text{CH}_2\text{R}$

R	Wt	Packing ^a	Temp	Press	Wt recovered	Products (VPC)
	g		C°	mm	g	
Br	3	A	500	760	2.5	37% $\text{C}_6\text{F}_5\text{OCHBrCH}_3$; 19% $\text{C}_6\text{F}_5\text{OH}$; 15% $\text{C}_6\text{F}_5\text{OCH}=\text{CH}_2$; 4% $\text{C}_6\text{F}_5\text{OCH}_2\text{CH}_2\text{Br}$; 2% $(\text{C}_6\text{F}_5\text{O})_2\text{CHCH}_3$.
Cl	1	A	520	760	0.75	70% $\text{C}_6\text{F}_5\text{OCH}_2\text{CH}_2\text{Cl}$; 5% $\text{C}_6\text{F}_5\text{OH}$; 5% $\text{C}_6\text{F}_5\text{OCH}=\text{CH}_2$; 1% $\text{C}_6\text{F}_5\text{OCClHCH}_3$.
OAc	1.3	A	560	760	.9	35% $\text{C}_6\text{F}_5\text{OH}$; 20% $\text{C}_6\text{F}_5\text{OCH}=\text{CH}_2$; 15% $\text{CH}_3\text{CO}_2\text{H}$; 20% 7-products.
OAc	1.3	A	600	0.8	1.0	75% $\text{C}_6\text{F}_5\text{OCH}_2\text{CH}_2\text{OAc}$; 10% $\text{C}_6\text{F}_5\text{OH}$; 3% $\text{C}_6\text{F}_5\text{OCH}=\text{CH}_2$; 2% $\text{CH}_3\text{CO}_2\text{H}$.
CF_3CO_2	2	A	540	25	1.6	70% $\text{C}_6\text{F}_5\text{OCH}_2\text{CH}_2\text{OAcF}_3$; 25% $\text{C}_6\text{F}_5\text{OH}$, $\text{CF}_3\text{CO}_2\text{H}$, $\text{C}_6\text{F}_5\text{OCH}=\text{CH}_2$.
OC_6F_5	3	A	480	760	2.6	70% $\text{C}_6\text{F}_5\text{OCH}_2\text{CH}_2\text{OC}_6\text{F}_5$; 14% $\text{C}_6\text{F}_5\text{OH}$.
OH	5	B	420	760	2.0	99% $\text{C}_6\text{F}_5\text{OH}$.
OH	3	B	300	760	1.2	99% $\text{C}_6\text{F}_5\text{OH}$.
OH	2	KHSO_4	220	50	1.7	No reaction.

^a Key: A, glass helices; B, Al_2O_3 pellets.

At 500 °C, the chlorine analog (table 1, R=Cl) is more stable than the bromine derivative, as a result, conversion was much lower. However, pentafluorophenol and pentafluorophenyl vinyl ether were formed in approximately equal quantities, along with a trace of 1-chloro-1-pentafluorophenoxyethane.

From the pyrolysis of the acetate (table 1, R=OAc), pentafluorophenol was usually the main product, with lesser quantities of the pentafluorophenyl vinyl ether and acetic acid, along with traces of five other products (unidentified). When the acetate was pyrolyzed under reduced pressure at different temperatures, no significant change in product distribution was observed, except that conversions were lower. At the same pressure (0.8 mm), a rise in the temperature from 550 to 600 °C simply increased the yield of pentafluorophenol, so higher temperatures were not further investigated. At a higher pressure (25 mm) and 540 °C, the pyrolysis of the acetate gave essentially the same products as observed at atmospheric pressure and 560 °C. The above acetate pyrolyses agree to some extent with those reported for 2-phenoxyethyl acetate [10]. In our case, the yield of pentafluorophenyl vinyl ether is higher and probably reflects the increased stability of the vinyl ether due to the ring fluorine atoms. As expected, no products were obtained which could be attributed to the Claisen [14] rearrangement. Although Ritchie [9] has reported benzaldehyde as one of the breakdown products of 2-phenoxyethyl acetate, we have been unable to isolate any pentafluorobenzaldehyde from the pyrolysis of 2-pentafluorophenoxyethyl acetate.

The pyrolysis of 2-pentafluorophenoxyethyl trifluoroacetate was expected to cause preferential cleavage at the alkyl-trifluoroacetate bond, to yield pentafluorophenyl vinyl ether in greater quantity. Actually, the additional fluorine atoms stabilized the compound, in

as much as only 30 percent conversion to products was obtained at 540 °C/25 mm pressure. Pentafluorophenol, pentafluorophenyl vinyl ether, and trifluoroacetic acid were formed in almost equal amounts. Since no selective cleavage was encountered, further pyrolyses of the acetates were not pursued.

The pyrolysis of 2-pentafluorophenoxyethanol (table 1, R=OH) over alumina at 300 or 420 °C resulted in the formation of pentafluorophenol and acetaldehyde. No dehydration to pentafluorophenyl vinyl ether was observed. Similar results have been reported [10] for 2-phenoxyethanol.

Potassium acid sulfate at 220 °C failed to dehydrate the alcohol, and no product other than 2-pentafluorophenoxyethanol was recovered.

In an attempt to explain some of the foregoing results, especially the formation of rearranged products, some additional pyrolyses were performed on compounds containing the pentafluorophenoxy group (table 2A). For comparison, some hydrocarbon samples (table 2B) were also included. It was first believed that some of the products were breakdown products of pentafluorophenyl vinyl ether. However, this compound (table 2A, R=CH=CH₂) does not show any appreciable decomposition until it is heated to 600 °C. Similarly, it was thought that 1,1-bis



(pentafluorophenoxy)ethane (table 2A, R=—CHCH₃), formed from the pyrolysis of 2-pentafluorophenoxyethyl bromide (table 1, R=Br), was produced by the addition of pentafluorophenol to pentafluorophenyl vinyl ether (eq 4, R=C₆F₅O—). However, the pyrolysis of a 50 percent mixture of the two (table 2A, R=CH=CH₂ and H) gave only starting materials. This mode of addition is not entirely without merit, since it was subsequently shown that 1,1-bis(penta-

TABLE 2. Comparison of the pyrolyses of C₆F₅OR and C₆H₅OR

R	Wt	Packing ^b	Temp	Wt recovered	Products
A. Pyrolysis of C ₆ F ₅ OR ^a					
CH=CH ₂	2	A	500	1.7	90% C ₆ F ₅ OCH=CH ₂ ; 5% C ₆ F ₅ OH
CH=CH ₂	2	A	600	1.6	60% C ₆ F ₅ OCH=CH ₂ ; 25% C ₆ F ₅ OH
CH ₃	2	A	525	1.6	95% C ₆ F ₅ OCH ₃ ; 2% C ₆ F ₅ OH
CH ₂ CH ₃	2	A	525	1.4	60% C ₆ F ₅ OCH ₂ CH ₃ ; 25% C ₆ F ₅ OH; 10% others
CH=CH ₂	0.8	A	525	1.6	50% C ₆ F ₅ OCH=CH ₂ ; 50% C ₆ F ₅ OH
H	1.0			2.0	
OC ₆ F ₅	2.5	A	520	2.0	49% C ₆ F ₅ OH; 49% C ₆ F ₅ OCH=CH ₂ ; 2% (C ₆ F ₅ O) ₂ CH—CH ₃
—CHCH ₃	2	A	500	1.8	80% C ₆ F ₅ OCH ₂ CF ₃ ; 5% C ₆ F ₅ OCH=CF ₂ ; 5% 7-products
CH ₂ CF ₃				2.5	
CH ₂ CF ₃	3	B	460	2.5	100% C ₆ F ₅ OCH ₂ CF ₃
B. Pyrolysis of C ₆ H ₅ OR ^a					
CH ₂ CH ₃	2	A	525	1.5	98% C ₆ H ₅ OCH ₂ CH ₃
CH=CH ₂	2	A	520	1.6	60% C ₆ H ₅ OCH=CH ₂ ; 25% C ₆ H ₅ OH
CH ₂ CH ₂ Br	25	A	400	20	98% C ₆ H ₅ OCHBr—CH ₃

^a All at atmospheric pressure.

^b Key: A, glass helices; B, charcoal pellets.

fluorophenoxy)ethane (table 2A, $R = -CHCH_3$) decomposes almost quantitatively to pentafluorophenol and pentafluorophenyl vinyl ether. The high yield of olefin formed in this pyrolysis was similar to that obtained by Reppe [11] for 1,1-diethoxyethane.

The other rearranged product obtained from the pyrolysis of 2-pentafluorophenoxyethyl bromide (table 1, $R = Br$) was 1-bromo-1-pentafluorophenoxyethane. Simply, this compound may have been formed as visualized in eqs 3 and 4. As yet, this has not been proved experimentally. The instability of α -halo ethers is well known. Surprisingly, the pyrolysis of 2-phenoxyethyl bromide (table 2B, $R = CH_2CH_2Br$) gave only the 1-bromo-1-phenoxyethane as the main product, similar to the behavior in the fluorocarbon series. The two isomeric bromides (hydrocarbon) differ greatly in chemical properties and can readily be distinguished by their behavior with water at room temperature. 1-Bromo-1-phenoxyethane decomposes spontaneously into a red resinous product, with the liberation of hydrogen bromide, by the addition of a trace of water. On the other hand, the 2-bromo derivative has little tendency toward this type of reaction. In the fluorocarbon series, 1-bromo-1-pentafluorophenoxyethane does not exhibit this readiness to react with water, unlike the hydrocarbon analog. However, on storage at 25 °C in the dark for several weeks, the 1-bromo-1-pentafluorophenoxyethane decomposes to a blackish mass. Unfortunately, 1-bromo-1-pentafluorophenoxyethane was not obtained in the pure state, so that its thermal stability has not been recorded.

5. Discussion

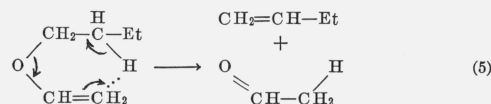
From the results of the pyrolysis of the fluoroaryl ethers listed in table 1, some generalizations are apparent. In these cases, where the reaction path could have proceeded in two directions, i.e., according to eqs 1 and 2, pentafluorophenol was usually obtained in greater quantity. The conversion into products at the temperatures employed also serves as a measure of the thermal stability of the alkyl fluoroaryl ethers. The results in tables 1 and 2 indicate that the pentafluorophenoxy group is a more effective leaving group when in competition with the other functional groups (R) shown. This effect appears to be associated with the number and activity of the β -hydrogen atoms in the molecule. In the pyrolysis of 2-pentafluorophenoxy-1,1,1-trifluoroethane (table 2A, $R = CH_2CF_3$) (a compound containing only α -hydrogen atoms with no hydrogen atoms β to the oxygen atom), no cleavage to pentafluorophenol was observed, but only dehydrofluorination to the olefin. Similarly, where the β -hydrogen atoms are attached to a double bond, as in pentafluorophenyl vinyl ether (table 2A, $R = CH=CH_2$), pentafluorophenol is formed at higher temperatures. However, pentafluorophenetole (table

2, $R = CH_2CH_3$) containing three β -hydrogen atoms, yields pentafluorophenol at lower temperatures. Pentafluoroanisole also yields a trace of pentafluorophenol, even though no β -hydrogen atoms are available (probably a bimolecular reaction, similar to that of anisole [15]).

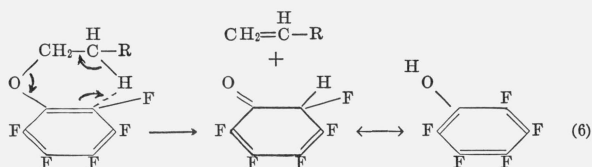
In the case of the isomeric bis(pentafluorophenoxy)ethanes (1,2 table 1, $R = OC_6F_5$ and 1,1 table 2A,

$R = -CHCH_3$), the position of the R group has a decided effect on the course of pyrolysis. Each pentafluorophenoxy group in the 1-position has three available β -hydrogen atoms for reaction, whereas, in the 1,2-derivative, each pentafluorophenoxy group has only two. On this basis, the 1,1-derivative would be the less stable. Also, the 1,1-derivative is an acetal containing two bulky groups, a situation which is in itself conducive to thermal decomposition at lower temperatures.

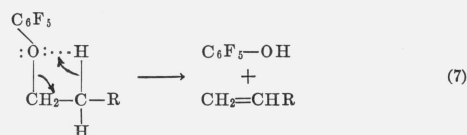
A considerable amount of data is available in the literature concerning the pyrolysis of ethers [9, 10, 15, 16], as well as of other types of compounds, such as esters, halides, and amides. The decomposition is for the most part considered to be unimolecular, and a cyclic mechanism was proposed [16]. Later work by Bailey [17, 18] and others [19] has shown the cyclic process to be the preferred route. Bailey [18] views the pyrolysis of vinyl ethers to occur as follows:



Certainly, a similar mechanism may be written for the fluoroaryl ethers,



An alternative mechanism may be written for the fluoroaromatic ethers, as follows:



This is similar to the mechanism for the decomposition of alkyl halides proposed by Maccoll [20]. In this case, the pentafluorophenyl group is not involved in the transfer of electrons, thereby preserving aromaticity; but a four-membered ring supersedes the more-favored six-membered ring. At present, since both mechanisms involve β -hydrogen atoms, the products may

be explained by either. The fact that no fluorophenols containing ring-hydrogen atoms were produced would indicate that hydrogen rather than fluorine migration occurs in eq 6, which is expected. The pyrolysis of a more varied group of ethers would be required in order to permit us to ascertain fully which mechanism is predominant.

The mechanism for the pyrolysis of the aryl perfluoroalkyl ethers is different from that reported here for the alkyl fluoroaryl ethers. Sheppard [21] has pyrolyzed a number of ethers (such as phenyl pentafluoroethyl ether), and has found that one of the primary pyrolytic products is biphenyl (not phenol). In these cases, cleavage occurs at the phenyl-oxygen link, not the alkyl-oxygen bond. The fact that fluorobenzene was also reported as one of the products at higher temperatures (625 °C) would indicate that the mechanism(s) for the decomposition of the aryl perfluoroalkyl ethers are more complex than those of the decomposition of the alkyl fluoroaryl ether type.

6. Basic Reagents

The reactions of some alkyl fluoroaryl ethers with potassium hydroxide are listed in table 3. These ethers could have reacted in any of several ways—(a) dehydrohalogenation to an olefin, (b) cleavage at the ether oxygen atom to a phenol, (c) attack on the ring fluorine atoms, or (d) various combinations of these. Information regarding the stability of these alkyl fluoroaryl ethers towards basic reagents may aid in elucidating the cleavage reaction found when pentafluoroanisole is treated with ammonia [4] or when the fluoro-dihydroxy compounds are obtained from the reaction of hexafluorobenzene with alcoholic potassium hydroxide [3]. From the limited number of reactions attempted, only the pentafluorophenoxyethyl bromide shows any reactivity below 200 °C.

TABLE 3. Reaction of C_6F_5OR with some bases

R	Wt	Base	Temp	Wt recovered	Products
CH_2CH_2Br	$\frac{g}{8.5}$	KOH (5) paraffin oil (5)	180	$\frac{g}{3.5}$	86% $C_6F_5OCH_2CH_2Br$, 14% C_6F_5OH .
CH_2CH_2Br	3	KOH (5) K_2CO_3 (10)	200	1.2	50% $C_6F_5OCH_2CH_2Br$, 50% $C_6F_5OCH=CH_2$.
CH_2CH_2Br	5	KOH (5) H_2O (20)	100	4.0	62% $C_6F_5OCH_2CH_2Br$, 37% C_6F_5OH .
CH_2CH_2Br	5	Collidine	160	3.0	83% $C_6F_5OCH_2CH_2Br$, 16% $C_6F_5OCH=CH_2$.
$\begin{array}{c} OC_6F_5 \\ \\ -CHCH_3 \end{array}$	0.4	KOH (1) H_2O (5)	100	0.3	No reaction.
CH_2CF_3	8.5	KOH (5) K_2CO_3 (10)	200	8.0	No reaction.
CH_2CF_3	1.4	MgO (5)	150	1.3	No reaction.
CH_2CF_3	20	20% KOH/charcoal	480	16	80% $C_6F_5OCH_2CF_3$, 15% $C_6F_5OCH=CF_2$.
CH_2CF_3	2	20% KOH/charcoal	550	Decomposed.
CF_2CF_2H	2	20% KOH/charcoal	550	Decomposed.

In this case, cleavage to pentafluorophenol is the main route, when potassium hydroxide and water (or paraffin oil) are used. Dehydrohalogenation was the preferred

course with solid potassium hydroxide pellets, yielding pentafluorophenyl vinyl ether. Similar results were obtained by Corley [22] with the latter reagent and with 2-chloro-1,1,2-trifluoroethyl phenyl ether. Here again, as proposed earlier [4], it appears that aqueous, basic systems preferentially lead to aryl ether cleavage. All of the ethers, the synthesis of which is described in this article, along with those prepared previously [4], were prepared in basic, nonaqueous solvents, and yet, little cleavage of the ether was observed.

2-Pentafluorophenoxy-1,1,1-trifluoroethane (table 3, $R = CH_2CF_3$) failed to react either with solid potassium hydroxide or magnesium oxide at 200 °C. Some olefin was formed by the use of 20 percent potassium hydroxide mounted on charcoal pellets at 480 °C. Higher temperatures decomposed the compound; this decomposition was also observed for 2-pentafluorophenoxy-1,1,2,2-tetrafluoroethane (table 3, $R = CF_2=CF_2H$).

The stability of 1,1-bis(pentafluorophenoxy)ethane toward aqueous potassium hydroxide was unexpected in view of the acidic hydrogen atom present because of the effect of the pentafluorophenoxy groups attached to the same carbon atom. This behavior toward aqueous bases is more analogous to that of such compounds as difluoromethyl ethyl ether [23] or difluoromethyl phenyl ether [24], rather than to that of an acetal.

7. Reactions in Acid

From the preceding sections, data were obtained regarding the stability of these fluoroaryl ethers under pyrolysis conditions or toward basic reagents. It was desired, therefore, to obtain data concerning their reactivity with sulfuric acid. Pentafluoroanisole [3] was shown to be cleaved with hydriodic acid to pentafluorophenol. Later, hydrobromic or aluminum chloride [25] was also found effective for this reaction. Recently, Tatlow and coworkers [26] have shown that 4-(trifluoromethyl)-2,3,5,6-tetrafluorophenetole cannot be cleaved preferentially without reaction at another part of the molecule [primarily due to the *p*-(trifluoromethyl) group]. Most of the ethers listed in table 4 are cleaved to pentafluorophenol under the reaction conditions. Only 2-pentafluorophenoxy-1,1,1-trifluoroethane (table 4, $R = CH_2CF_3$) failed to yield any product. The stability of this compound is probably associated with the decrease in basicity of the oxygen linkage due to the added trifluoromethyl group. Cleavage of ethers by acids is usually preceded by oxonium salt formation. The fact that 1,1-bis(pentafluorophenoxy)ethane (table 4, $R = \begin{array}{c} OC_6F_5 \\ | \\ -CHCH_3 \end{array}$) decomposes under these conditions is not surprising, since the trifluoromethyl group is a more effective electro-

negative group than the pentafluorophenoxy group. As such, the lessening in oxygen basicity is not sufficient to prevent oxonium salt formation and eventual cleavage.

TABLE 4. Reaction of C₆F₅OR with sulfuric acid at 125 °C

R	Wt	H ₂ SO ₄	Wt recovered	Products
	g	ml	g	
CH ₃ CH ₂ Br	1	7	0.5	99% C ₆ F ₅ OH.
CH ₃ CF ₃	3	7	2.7	No reaction.
CH ₂ =CH ₃	5	10	3.2	60% C ₆ F ₅ OH, 40% C ₆ F ₅ OCH ₂ CH ₃ .
CH ₂ CH ₂ OH	1.5	7	1	50% C ₆ F ₅ OH, 50% C ₆ F ₅ OCH ₂ CH ₂ OH.
$\begin{array}{c} \text{OC}_6\text{F}_5 \\ \\ \text{—CHCH}_3 \end{array}$	0.3	1	Decomposed, some C ₆ F ₅ OH.

8. Polymerizations

In an earlier report [1], the polymerization of phenyl and pentafluorophenyl 1,1,2-trifluorovinyl ethers was described. Usually, cationic or peroxide-initiated catalysis of the monomers gave little or no polymer. However, by the use of high pressure and γ -irradiation [27], these monomers were converted into low molecular weight polymers ($\text{DP}_n \sim 4000$).

In line with the above results, 1,2-difluorovinyl pentafluorophenyl ether failed to yield any polymer with azobis(isobutyronitrile) (ABIN). Thermally (at 110 °C), it appears that only the dimer was formed. As yet, no high-pressure techniques have been employed in the polymerization of this monomer.

Pentafluorophenyl vinyl ether appears to be a more reactive monomer. A white, solid polymer can be obtained from pentafluorophenyl vinyl ether in pentane solution by the use of boron trifluoride gas at -78 °C. After 24 hr under these conditions, the conversion into polymer was 17 percent and the molecular weight (vapor pressure osmometer) was 10,000 (mp 75 – 88 °C). Higher conversion (30%) and polymers having increased molecular weights (17,000) were obtained by longer storage times (7 days) at -78 °C and by periodic addition of the catalyst, boron trifluoride–water. Some observations made during this latter process appear to indicate that the proportion of the co-catalyst (water) has more effect on the conversion into polymers than either an excess of boron trifluoride or longer reaction times. After 3 days, the amount of polymer formed is approximately the same as after the 24-hr period, but polymer formation again appears to increase when additional water or moisture is introduced. The polymer obtained in this fashion (17,000 mol wt) was a hard, white solid. It is soluble in benzene, hexafluorobenzene, and acetone. The polymer is insoluble in methanol and in water. Also, the melting point, 55 to 60 °C, is lower than that of the polymer of 10,000 mol wt.

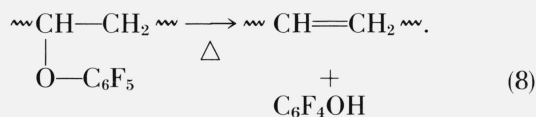
Aluminum chloride and pentafluorophenyl vinyl ether in bulk at 35 °C gave only blackish tars. However, a low molecular weight polymer was obtained when the polymerization was performed in benzene solution at 80 °C. Methanol was used to precipitate the polymer. The molecular weight was 2300 as determined with a vapor-pressure osmometer (benzene as solvent). The polymer thus obtained was a

yellow glass which melted over the range 120 to 180 °C. The low molecular weight of the polymer is in accord with recent observations [28] concerning the polymerization of various mono- and di-halogenated phenyl vinyl ethers.

Cationic reagents, such as concentrated hydrobromic acid, have no effect on pentafluorophenyl vinyl ether. This is in contrast to the behavior of phenyl vinyl ether, which yields resinous materials after a slight induction period. Similar material was obtained by the addition of water to 1-bromo-1-phenoxyethane.

Again, by the use of high pressure (9500 atm) and γ -irradiation (0.009 Mr/hr) at 105 °C for 68 hr, a poly(pentafluorophenyl vinyl ether) having a molecular weight of 30,000 (vapor-pressure osmometry) was obtained in low yield. The polymer was a fluffy, pink solid, softening at 95 °C and melting below 150 °C.

Pyrolysis of the poly(pentafluorophenyl vinyl ether), 17,000 mol wt, at 300 °C for 1 hr resulted in a 43.2 percent weight loss, and yielded mainly pentafluorophenol and a dark-brown glassy residue. The low order of thermal stability of this polymer was in accord with the results obtained from the pyrolysis of the smaller molecule.



The thermal stability of the poly(phenyl trifluorovinyl ether), 4,000 mol wt [29], was shown to be greater than that of the poly(pentafluorophenyl vinyl ether) reported here. Since there are no hydrogen atoms on the polymer backbone in the former, phenol cannot be readily removed. However this polymer loses hydrogen fluoride quite readily, and this is followed by cross-linking and carbonization. Presumably, the removal of hydrogen fluoride is an intermolecular process. From the preceding evidence, it is, therefore, reasonable to assume that the poly(pentafluorophenyl 1,1,2-trifluorovinyl ether) prepared previously [1] should have good thermal stability, since there is no ready route to decomposition as experienced above, especially in the absence of hydrogen atoms. The difficulty still remains in producing polymers of high molecular weight.

9. Experimental Procedure

Infrared spectra were obtained with a Perkin-Elmer "Infracord," Model 137B spectrophotometer,³ using a 0.025-mm sodium chloride cell for liquid samples, or pellets containing 1–2 mg of the solid sample in 300 mg of potassium bromide. Molecular-weight

³ Certain commercial materials and equipment are identified in this paper in order to adequately specify the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Bureau of Standards, nor does it imply that the material or equipment identified is necessarily the best available for the purpose.

determinations were made by vapor-pressure osmometry, using a 1-percent solution of the polymer in benzene.

9.1. 2-Pentafluorophenoxyethyl Bromide

a. In *N,N*-Dimethylformamide

A solution of 50 g (0.23 mole) of potassium pentafluorophenoxide in 100 ml of *N,N*-dimethylformamide was added to a solution of 50 g (0.27 mole) of 1,2-dibromoethane in 100 ml of *N,N*-dimethylformamide maintained at 90 °C. After a slight induction period, potassium bromide began to be precipitated and this increased with time. When the addition was complete (0.5 hr), the contents were refluxed for 2 hr, cooled, and poured into 500 ml of water. The bottom layer was separated and dried (CaSO₄). Distillation of the products afforded 30 g (46%) of 2-pentafluorophenoxyethyl bromide, (bp 112 °C/10 mm, $n_D^{20} = 1.4647$) and 9.82 g (11%) of 1,2-bis(pentafluorophenoxy)ethane (bp 108–110 °C/0.8 mm, mp 31–32 °C).

Analysis: Calculated for C₈H₄BrF₅O: C, 33.0; H, 1.4; F, 32.7; Br, 27.5. Found: C, 33.6; H, 1.3; F, 31.0; Br, 24.5.

Analysis: Calculated for C₁₄H₄F₁₀O₂: C, 42.9; H, 1.0. Found: C, 42.8; H, 1.3.

b. In Tetrahydrofuran

A solution of 11 g (0.05 mole) of potassium pentafluorophenoxide and 19 g (0.1 mole) of 1,2-dibromoethane in 100 ml of tetrahydrofuran was refluxed for 18 hr. Very little potassium bromide was noticed. At the end of this time period, the mixture was cooled and poured into 200 ml of water. The bottom layer was separated, dried (CaSO₄), and distilled. After removal of 10 g of recovered 1,2-dibromoethane, 1.5 g (10.4%) of 2-pentafluorophenoxyethyl bromide was obtained. No 1,2-bis(pentafluorophenoxy)ethane was isolated from this reaction.

9.2. 2-Pentafluorophenoxyethyl Chloride

To 18 g (0.2 mole) of 1,2-dichloroethane in 25 ml of *N,N*-dimethylformamide at 80 °C was added 5 g (0.025 mole) of potassium pentafluorophenoxide in 25 ml of *N,N*-dimethylformamide. When the addition was complete (0.5 hr), the mixture was refluxed for 1 hr, cooled, and diluted with 150 ml of water. The usual isolation and distillation gave 3.1 g (56%) of 2-pentafluorophenoxyethyl chloride, bp 74–75 °C/2 mm; $n_D^{20} = 1.4442$.

Analysis: Calculated for C₈H₄ClF₅O: C, 39.0; H, 1.6; Cl, 14.3. Found: C, 40.1; H, 1.9; Cl, 12.9.

9.3. 1,1-Bis(pentafluorophenoxy)ethane

To 21.9 (0.11 mole) of 1,1-dibromoethane in 25 ml of *N,N*-dimethylformamide at 90 °C was added 5 g (0.025 mole) of potassium pentafluorophenoxide in 25 ml of *N,N*-dimethylformamide. After the addition (0.25 hr), the solution was refluxed for 4 hr, cooled, and diluted

with 150 ml of water. The usual processing, followed by distillation, yielded 0.9 g (10%) of 1,1-bis(pentafluorophenoxy)ethane, bp 84 to 85 °C/0.6 mm, mp 25–27 °C.

Analysis: Calculated for C₁₄H₄F₁₀O₂: C, 42.7; H, 1.0. Found: C, 43.4; H, 1.5.

9.4. 2-Pentafluorophenoxy-1,1,1-trifluoroethane

To 100 g (1 mole) of 1,1,1-trifluoroethanol in 250 ml of tetrahydrofuran, 22.9 g (1 g-atom) of sodium was added in small pieces. When the evolution of hydrogen had ceased, the solution was added dropwise to a solution of 250 g (1.35 moles) of hexafluorobenzene in 125 ml of pyridine, maintained at 80 °C. When the addition was complete (2 hr), the mixture was refluxed for 2 hr. The mixture was cooled, and filtered from the sodium fluoride. The filtrate was poured into 500 ml of 10 percent hydrochloric acid. The bottom layer was separated and dried (CaSO₄). Distillation afforded: 82 g (33%) of recovered hexafluorobenzene; 159 g (66.2%, based on recovered C₆F₆) of 2-pentafluorophenoxy-1,1,1-trifluoroethane, bp 146.5–147 °C; $n_D^{23} = 1.3799$; and 34 g (10.9% based on recovered C₆F₆) of 1,4-bis(1,1,1-trifluoroethoxy)tetrafluorobenzene, bp 111 to 113 °C/10 mm, mp 67 to 69 °C.

Analysis: Calculated for C₈H₂F₈O: C, 36.3; H, 0.76; F, 57.2. Found: C, 36.4; H, 0.7; F, 56.2.

Analysis: Calculated for C₁₀H₄F₁₀O₂: C, 34.8; H, 1.2; F, 55.0. Found: C, 34.8; H, 1.2; F, 53.9.

9.5. Pentafluorophenetole

Pentafluorophenetole was prepared in much the same manner as reported previously [5], except that the following quantities were used: 150 ml of absolute ethanol, 150 ml of tetrahydrofuran, 22.9 (1 g-atom) of sodium metal, 250 g (1.35 moles) of hexafluorobenzene, and 125 ml of pyridine. Pentafluorophenetole was obtained in 74 percent yield (144 g), bp 152 to 153 °C, $n_D^{23} = 1.4120$.

9.6. 2-(Pentafluorophenoxy)ethanol

A solution of 25 g (0.2 mole) of 2-bromoethanol in 25 ml of tetrahydrofuran was added to a solution of 36 g (0.16 mole) of potassium pentafluorophenoxide in 100 ml of tetrahydrofuran at 64 °C. The mixture was refluxed for 3 hr and cooled. The usual processing afforded 16 g (53%, based on recovered C₆F₅OH, 6 g) of 2-(pentafluorophenoxy)ethanol, bp 82 to 83 °C/1.5 mm, $n_D^{23} = 1.4419$. (Reported [7] bp 110 °C/15 mm). In the infrared spectrum, the absorption band (OH frequency) is at 3490 cm⁻¹.

Analysis: Calculated for C₈H₅F₅O₂: C, 42.2; H, 2.2. Found: C, 41.6; H, 2.3.

9.7. 2-(Pentafluorophenoxy)ethyl Acetate

To 5 g (0.02 mole) of 2-(pentafluorophenoxy)ethanol and 5 g (0.05 mole) of acetic anhydride was added 0.1 g

of potassium acetate, and the solution was refluxed for 2 hr. The mixture was cooled, and poured into 50 ml of ice water. The solution was neutralized by the addition of saturated sodium hydrogen carbonate solution. The bottom layer was washed with 25 ml of water, separated, dried (CaCl_2), and distilled. 2-(Pentafluorophenoxy)ethyl acetate was obtained in 71 percent yield, bp 90–91 °C/1.5 mm, $n_D^{20}=1.4352$. (In the infrared spectrum there was an absorption band, $\nu_{\text{C=O}}$, at 1740 cm^{-1} .)

Analysis: Calculated for $\text{C}_{10}\text{H}_7\text{F}_5\text{O}_3$: C, 45.3; H, 2.6. Found: C, 44.6; H, 2.5.

9.8. 2-(Pentafluorophenoxy)ethyl Trifluoroacetate

This compound was prepared as described above. From 5 g (0.02 mole) of 2-(pentafluorophenoxy)ethanol, 5 g of trifluoroacetic anhydride, and 0.1 g of potassium carbonate, there was obtained 5 g (70%) of 2-(pentafluorophenoxy)ethyl trifluoroacetate, bp 88 to 89 °C/1.5 mm, $n_D^{20}=1.4048$. (Infrared spectrum showed a band, $\nu_{\text{C=O}}$, at 1780 cm^{-1} .)

Analysis: Calculated for $\text{C}_{10}\text{H}_4\text{F}_8\text{O}_3$: C, 37.8; H, 1.24. Found: C, 37.8; H, 1.20.

9.9. Pentafluorophenyl Vinyl Ether

Eighty-two grams (0.45 mole) of pentafluorophenol, 5 g of potassium hydroxide, and 150 ml of *N,N*-dimethylacetamide were placed in a 1400-ml bomb which was then sealed. The bomb was attached to a high-vacuum line by an outlet valve and tubing. After cooling (–190 °C) and evacuating the bomb, 13.62 g (0.61 mole) of acetylene gas was condensed in the bomb, which was then sealed and allowed to warm to 25 °C. The bomb was rocked and heated to 200 °C (at this temperature, the maximum pressure was 160 psi) for 1.5 hr or until no change in pressure was observed. The bomb was cooled and excess acetylene was allowed to escape. The contents was poured into 200 ml of water and extracted several times with 100-ml portions of dichloromethane. The organic layers were combined and dried (CaSO_4). After removal of the solvent by distillation, there was obtained 47.4 g (50%) of pentafluorophenyl vinyl ether, bp 141 to 142 °C, $n_D^{20}=1.4252$. The infrared spectrum shows the olefin bond at 1640 cm^{-1} .

Analysis: Calculated for $\text{C}_8\text{H}_3\text{F}_5\text{O}$: C, 45.8; H, 1.44. Found: C, 46.3; H, 1.50. From the residue, 1,1-bis(pentafluorophenoxy)ethane (10%) was obtained; this had the characteristics described earlier. Small amounts of other products were also obtained, but these were not investigated.

9.10. Phenyl Vinyl Ether

This compound was prepared as described by Ritchie [9], from 2-(pentafluorophenoxy)ethyl bromide and potassium hydroxide.

9.11. 1,2-Difluorovinyl Pentafluorophenyl Ether

An 800-ml bomb containing 100 g (0.45 mole) of anhydrous potassium pentafluorophenoxide, 300 ml of dry benzene, and 100 ml of dry (LiAlH_4) tetrahydrofuran was attached to a high-vacuum line, cooled (–196 °C), and evacuated. In the bomb was condensed 110 g (1.34 moles) of 1,1,2-trifluoroethylene by means of the vacuum line. The sealed bomb was allowed to warm to 25 °C. It was then rocked and heated to 230 °C, at which temperature the pressure dropped from 1600 psi to 800 psi during 1 hr. The bomb was cooled and opened. The contents was poured into a flask and the liquids were flash-distilled. The residual solids were washed with benzene (100 ml), the benzene layer was combined with the flash distillate, and the liquid was distilled. After the solvents had been removed, there was obtained 36 g of a colorless liquid, bp 133 to 139 °C, which contained 90 percent of 1,2-difluorovinyl pentafluorophenyl ether. A pure sample of this ether was obtained by preparative, vapor-phase chromatography, using a 20 percent Viton A-Celite (see footnote 3) column at 150 °C. The pure vinyl ether (bp 132–132.5 °C, $n_D^{23}=1.3940$, showing $\nu_{\text{CF=CFH}}$ at 1786 cm^{-1} in the infrared spectrum) was eluted first. The impurity appears to be mainly the saturated ether, pentafluorophenyl 1,1,2-trifluoroethyl ether, bp 155 to 158 °C (impure).

9.12. Pyrolysis Procedure

The pyrolysis apparatus consisted of a Pyrex tube, 45 cm long and 1 cm wide, having a female $14/20$ joint at the top and a male $14/20$ joint at the bottom. A pressure-equalizing, 25-ml, addition funnel was placed at the top of the tube. The top of the funnel was connected to the nitrogen gas-inlet system. To the bottom end of the pyrolysis tube was fitted a $14/20$ jointed connector which had take-offs to the first and second traps. The second trap was usually connected to a drying tube (atmospheric pressure experiments) or to a vacuum pump for experiments under reduced pressure. Both traps were cooled by solidified carbon dioxide acetone mixtures. The packing (5-in. cross section) was usually supported by a constriction in the glass tube. The tube was heated by a tube furnace to the desired temperature, and the compounds were added dropwise from the addition funnel. The nitrogen flow-rate was usually 3.5 cm^3/min . Other conditions are listed in tables 1 and 2. The first trap usually contained most of the pyrolyzate. Upon warming, a sample of the pyrolyzate was analyzed by vapor-phase chromatography, using columns of 20 percent silicone oil on Celite. Identification of the components of the pyrolyzate was made by comparison of the retention times with those of known samples. The relative percentage composition of the pyrolyzate was obtained from the peak height and width of the individual components.

9.13. Basic Reagents

The details are listed in table 3. The compound and the aqueous potassium hydroxide were mixed at 25 °C, heated at 100 °C for 1 hr, and cooled, and the aqueous solution was extracted with dichloromethane to remove the neutral compounds. Acidification of the basic layer with 10 percent hydrochloric acid gave pentafluorophenol. Where potassium hydroxide pellets were used, a bed of solid potassium carbonate was employed, to protect the glass surface during the reaction. The KOH-K₂CO₃ mixture was heated to 200 °C before the sample was added dropwise. The sample was then refluxed from the KOH-K₂CO₃ mixture for 30 min before allowing distillation to proceed. Cleavage products, usually pentafluorophenol, were obtained by acidification of the base after dilution with water. Pyrolyses over 25 percent KOH-charcoal pellets were accomplished in the same apparatus as described above. Products were identified by vapor-phase chromatography.

9.14. Acid Reactions

Concentrated sulfuric acid (98%) was the only acid employed in these reactions, listed in table 4. The acid and the compound were mixed at room temperature, and heated at 125 °C for 1 hr. Most of the compounds were immiscible with the reagent, and, occasionally, shaking and swirling were necessary. The products were isolated by cooling the reactants to 0 °C and adding crushed ice to the acid solution. The fluorocarbon layer could be separated from the aqueous layer. Again, identification of the products was made by vapor-phase chromatography.

9.15. Polymerization Reactions

a. Pentafluorophenyl Vinyl Ether

(1) *With α,α -Azobis(isobutyronitrile) (ABIN).* To 1 g of pentafluorophenyl vinyl ether in a Pyrex tube was added 0.01 g of ABIN. The tube was attached to a high-vacuum line and the contents degassed before the tube was sealed. It was then placed in a bath maintained at 60 °C. After 24 hr, only a slight yellow color had developed. The temperature was raised to 130 °C. After 7 days, the color was a darker yellow, but no polymerization had occurred. Recovered monomer (97%) was the main material. Only a trace of a brown solid was obtained; this was not investigated.

(2) *With Aluminum Chloride.* To 0.01 g of anhydrous aluminum chloride was added a solution of 1 g of pentafluorophenyl vinyl ether in 5 ml of anhydrous benzene. No reaction was observed at 25 °C. The solution was warmed to 50 °C, and an additional 0.01 g of aluminum chloride was added. An orange color now developed, and after refluxing the mixture for 2 hr, the color changed to deep purple. After cooling to 25 °C, 50 ml of methanol was added to the benzene solution, and the polymer was allowed to settle.

The polymer was a yellow, glassy material, mp 120 to 180 °C, and its molecular weight was 2300 (VPO).

(3) *With Boron Trifluoride.* A solution of 3 g of pentafluorophenyl vinyl ether and 25 ml of pentane in a 50-ml flask was saturated with boron trifluoride gas. The flask was then sealed, and stored at -78 °C for 3 days; some white solid had then precipitated. Three drops of water were added to the mixture, and the mixture was sealed, and stored at -78 °C for 4 days. The tube was opened, and nitrogen was bubbled through the solution to remove the excess boron trifluoride as gas. The tan, solid polymer was removed by filtration, and dried under vacuum. The filtrate yielded 2 g of recovered monomer. The dried polymer weighed 0.9 g (30% conversion). The poly(pentafluorophenyl vinyl ether) was dissolved in 25 ml of benzene and filtered. The benzene solution was added to 20 ml of methanol, and the white precipitate allowed to settle. After filtration and vacuum drying, the white polymer weighed 0.31 g (mp 55 to 60 °C). It was soluble in benzene, hexafluorobenzene, and acetone. The molecular weight (VPO) was 17,000.

b. 1,2-Difluorovinyl Pentafluorophenyl Ether

Into each of two quartz tubes was placed 1 g of 1,2-difluorovinyl pentafluorophenyl ether, and each tube was sealed. One of the tubes also contained 0.01 g of ABIN. Both tubes were irradiated at 25 °C for 3.5 days with an ultraviolet lamp at a distance of 10 in. No reaction was visible. The tubes were then kept in a furnace at 110 °C for 4 days. At the end of this period, the contents of both tubes were black and viscous. Some solid was observed in both tubes. The tube containing ABIN had twice as much black liquid as the blank tube. The products of these reactions appear to be mainly dimers.

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